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(54) **Cured silicone powder and process for the preparation thereof.**

(57) There is disclosed a process comprising

(I) preparing a water-based dispersion of

(A) a cured silicone powder having a number average particle diameter of 0.1 to 200 micrometers and

(B) an amorphous silica micropowder that has an average particle diameter not exceeding 1 micrometer and a surface silanol group density of at least 2 silanol groups per one nm² (100 square angstroms);

(II) heating said water-based dispersion; and

(III) removing the water from said dispersion, thereby producing a cured silicone rubber composition wherein the silica micropowder is immobilized on the surface of the cured silicone powder.

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The invention relates to a highly flowable and dispersible cured silicone powder that has minimal tendency to aggregate or undergo blocking. The invention also relates to a process for preparing said cured silicone powder.

Cured silicone powders are used as additives in cosmetics, paints, inks, thermosetting organic resins, thermoplastic organic resins, and so forth. They are useful as internal stress-relaxing agents for thermosetting (i.e., non-silicone) organic resins and as surface lubricants for organic resin films. These powders are fabricated by first preparing a water-based emulsion of a curable silicone composition (hereinafter a water-based curable SC emulsion), then curing the composition to form a water-based dispersion of a cured silicone powder, and finally removing water from the water-based dispersion (refer to JP-A 63-77942 and 64-70558).

However, the cured silicone powders represented by this art exhibit a poor fluidity and substantial aggregation or blocking tendencies. Moreover, these prior art powders are poorly dispersible in organic resins and organic solvents.

Other prior art approaches to this problem include JP-A4-348143 and JP-A 5-179144. The first of these teaches a method for preparing a cured silicone powder in which a silicon oxide sol is added to a water-based dispersion of a cured silicone powder (hereinafter a water-based cured SP dispersion) with the subsequent dewatering of the resultant mixture. The second claims a method for preparation of a simple powder mixture which consists of dewatering of a water-based dispersion of a cured silicone powder plus an inorganic micropowder. The resulting compositions still exhibit inadequate flow, dispersion, aggregation, and blocking characteristics. Other drawbacks with these approaches include the introduction of impurities, the separation or removal of the inorganic micropowders from the cured silicone powder, the inadequate response to shear forces, and the like.

The present invention introduces a highly flowable and highly dispersible cured silicone powder that exhibits little tendency to aggregate or undergo blocking. An additional object of the invention is the introduction of a process for preparing said cured silicone powder.

It comprises the combination of

(A) a cured silicone powder having an average particle diameter of 0.1 to 200 micrometers that has immobilized on its surface

(B) an amorphous silica micropowder that has an average particle diameter not exceeding 1 micrometer and a surface silanol group density of at least 2 silanol groups per one nm² (100 square angstroms).

The process of the present invention also provides a method for the preparation of this composition.

The characteristic feature of our invention consists of the anchorage or immobilization of the amorphous silica micropowder (B) on the surface of the cured silicone powder (A). Component (A) of the invention must be a cured silicone powder with an average (number average) particle diameter of 0.1 to 200 micrometers. The basis for this range is as follows: the amorphous silica micropowder (B) does not become satisfactorily anchored or immobilized on the surface of component (A) having an average particle diameter below 0.1 micrometer, while the final cured silicone powder product has a strongly reduced fluidity and dispersibility when component (A) has an average particle diameter in excess of 200 micrometers. The nature of component (A) is not critical and it may be a gel, rubber, or cured resin, with rubbers being preferred. The shape of component (A) is also not critical and it may be spherical, disk or amorphous shape. A spherical shape is preferred.

Component (B) of the invention is an amorphous silica micropowder that has an average particle diameter not exceeding 1 micrometer and a surface silanol group density of at least 2 silanol groups per one nm² (100 square angstroms). Component (B) will not become strongly anchored on the surface of cured silicone powder (A) when the average particle diameter of component (B) exceeds 1 micrometer or when its surface silanol group density is less than 2 silanol groups per one nm² (100 square angstroms). The shape of component (B) is not critical, but it is preferably spherical. The amorphous silica micropowder, component (B), is exemplified by dry-process, electric arc, and wet-process amorphous silica micropowders. Fumed silica, which is prepared by a dry process, is particularly preferred as component (B).

The initial step according to the present invention consists of the preparation of a water-based dispersion of the cured silicone powder (A). Typically, a curable silicone composition is first formulated into a water-based emulsion and the particles of curable silicone composition in the emulsion are then cured.

Any heretofore known curable silicone composition may be employed as the curable silicone composition of the preparative process of this invention. Examples of said curable silicone composition are addition reaction-curing silicone compositions, condensation reaction-curing silicone compositions, organoperoxide-curing silicone compositions, and ultraviolet-curing silicone compositions. Addition reaction-curing and condensation reaction-curing silicone compositions are preferred for their ease of handling.

The addition reaction-curing silicone compositions are exemplified by compositions that contain, as essential components,

(a) organopolysiloxane having at least 2 alkenyl groups in each molecule,

(b) organohydrogenpolysiloxane having at least 2 silicon-bonded hydrogen atoms in each molecule, and

5 (c) platinum catalyst,

and, as optional components,

(d) filler

and

(e) epoxy-functional organic compound or aryl group-containing organic compound.

10 Component (a) is the base component of such addition reaction-curing silicone compositions, and it consists of organopolysiloxane having at least 2 alkenyl groups in each molecule. This alkenyl group is exemplified by vinyl, allyl, propenyl, butenyl, pentenyl, hexenyl, and decenyl, with the vinyl group being preferred. The alkenyl group may be bonded at any position in the component (a) molecule, but is preferably bonded at the molecular chain terminals because this affords a particularly good curability. The non-alkenyl silicon-bonded organic groups in component (a) are monovalent hydrocarbon groups, e.g., alkyl groups such as methyl, ethyl, propyl, and butyl; cycloalkyl groups such as cyclopentyl, and cyclohexyl; aryl groups such as phenyl, tolyl, and xylyl; aralkyl groups such as benzyl, phenethyl, and 3-phenylpropyl; and halohydrocarbon groups such as 3-chloropropyl, or 3,3,3-trifluoropropyl. The molecular structure of component (a) is not critical and is exemplified by straight chain, cyclic, network, partially branched straight chain, and mixtures of such structures. Straight chain structures are preferred for the preparation of cured product in gel or rubber form. The viscosity of component (a) at 25 °C is not specifically restricted, and component (a) may have any viscosity that will permit the formation of a water-based emulsion the addition reaction-curing silicone composition. In specific terms, the viscosity may range from 1 mPa.s (centipoise) to that of high-viscosity gums. Preferred viscosities fall in the range of 20 to 100,000 mPa.s (centipoise) and particularly preferred viscosities fall in the range of 20 to 10,000 mPa.s (centipoise).

Component (b) is a crosslinker for the addition reaction-curing silicone composition, and it consists of organohydrogenpolysiloxane having at least 2 silicon-bonded hydrogen atoms in each molecule. The silicon-bonded organic groups in component (b) are monovalent hydrocarbon groups, e.g., alkyl groups such as methyl, ethyl, propyl, and butyl; cycloalkyl groups such as cyclopentyl, and cyclohexyl; aryl groups such as phenyl, tolyl, and xylyl; aralkyl groups such as benzyl, phenethyl, and 3-phenylpropyl; and halohydrocarbon groups such as 3-chloropropyl, or 3,3,3-trifluoropropyl. The silicon-bonded hydrogen may be bonded at any position in the component (b) molecule. The molecular structure of component (b) is not critical and is exemplified by straight chain, cyclic, network, partially branched straight chain, and mixtures of such structures. The viscosity of component (b) at 25 °C is not specifically restricted, and component (b) may have any viscosity that will permit the formation of a water-based emulsion by the addition reaction-curing silicone composition. In specific terms, viscosities in the range of 1 to 10,000 mPa.s (centipoise) are preferred. The quantity of component (b) is not specifically restricted as long as it is added in a quantity sufficient to induce cure of the addition reaction-curing silicone composition. The specifically preferred level is 0.3 to 100 weight parts of component (b) per 100 weight parts of component (a).

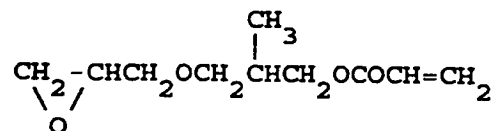
Component (c) is a platinum catalyst whose purpose is to accelerate the addition reaction between the alkenyl groups in component (a) and the silicon-bonded hydrogen atoms in component (b). The known platinum catalysts can be used as component (c), such as chloroplatinic acid, alcohol solutions of chloroplatinic acid, chloroplatinic acid-olefin complexes, chloroplatinic acid-alkenylsiloxane complexes, platinum black, and platinum-on-silica. The quantity of component (c) is not specifically restricted as long as it is added in a quantity sufficient to accelerate the addition reaction of the addition reaction-curing silicone composition. The specifically preferred addition is 1×10^{-7} to 1×10^{-3} weight parts as platinum metal in component (c) per 100 weight parts component (a).

A filler (d) can be added on an optional basis to the addition reaction-curing silicone composition in order to adjust the fluidity of the composition and/or improve the mechanical strength of the cured silicone powder product. Component (d) is exemplified by reinforcing fillers such as precipitated silica, fumed silica, calcined silica and, fumed titanium oxide; or by nonreinforcing fillers such as quartz powder, diatomaceous earth, aluminosilicates, iron oxide, zinc oxide, and calcium carbonate. Component (d) may be added directly to the addition reaction-curing silicone composition, or it may be added after a preliminary surface treatment with an organosilicon compound such as hexamethyldisilazane, trimethylchlorosilane, and polydimethylsiloxane.

In order to improve the affinity and adherence between organic resins and compositions of our invention, the addition reaction-curing silicone composition may optionally contain a component (e) that consists of an epoxy-functional or aryl group-containing organic compound. The epoxy-functional organic

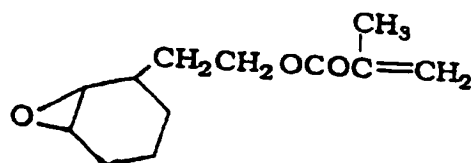
compounds contemplated are allyl glycidyl ether, vinylcyclohexene monoxide, glycidyl acrylate, glycidyl methacrylate, and compounds having the following formulae:

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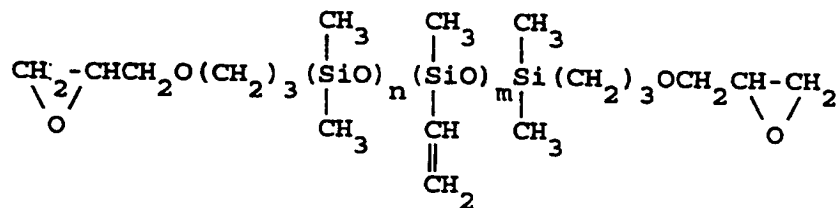
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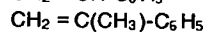
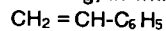


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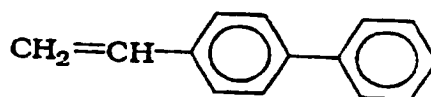
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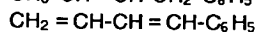
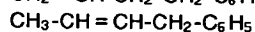
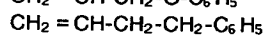
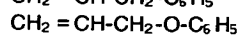
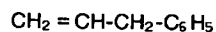
where n and m are each positive integers. The aryl group-containing organic compounds are exemplified by the following, in which -C₆H₅ represents the phenyl group.



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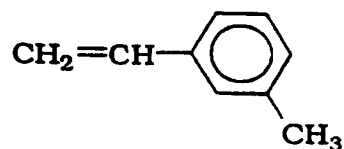


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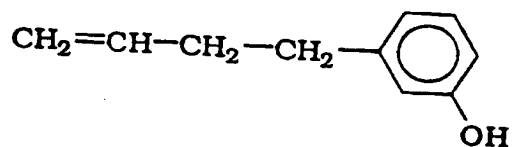


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Component (e) may be added to the mixing process for components (a), (b), and (c), or it may be preliminarily reacted with component (b). The quantity of component (e) is not critical, and component (e) should be added in the particular quantity that provides an excellent affinity between the cured silicone powder product and organic resins. The specifically preferred range is 0.1 to 50 weight parts per 100 weight parts component (a).

In order to control the cure rate, our addition reaction-curing silicone composition may contain a small quantity of an addition reaction inhibitor, such as an acetylenic compound, a hydrazine, a triazole, a phosphine, and a mercaptan. Other components that may be added to the subject addition reaction-curing silicone composition on an optional basis are pigments, heat stabilizers, flame retardants, photosensitizers, and diorganopolysiloxane that carries alkenyl only at one molecular chain terminal.

The contemplated condensation reaction-curing silicone compositions are exemplified by compositions that contain, as essential components,

(a') silanol-endsblocked organopolysiloxane,

(b') organohydrogenpolysiloxane having at least 2 silicon-bonded hydrogen atoms in each molecule, and

(c') condensation-reaction catalyst,

and, as optional components,

(d') filler

and

(e') silane coupling agent.

Component (a') is the base component of such condensation reaction-curing silicone compositions, and it consists of silanol-endsblocked organopolysiloxane. The silicon-bonded organic groups in component (a') are monovalent hydrocarbon groups, e.g., alkyl groups such as methyl, ethyl, propyl, and butyl; alkenyl groups such as vinyl, allyl, propenyl, butenyl, pentenyl, hexenyl, and decenyl; cycloalkyl groups such as cyclopentyl, or cyclohexyl; aryl groups such as phenyl, tolyl, and xylyl; aralkyl groups such as benzyl, phenethyl, and 3-phenylpropyl; and halohydrocarbon groups such as 3-chloropropyl, or 3,3,3-trifluoropropyl. The molecular structure of component (a') is not critical and is exemplified by straight chain, cyclic, network, partially branched straight chain, and mixtures of such structures. Straight chain structures are preferred for the preparation of cured product in gel or rubber form. The viscosity of component (a') at 25 °C is not specifically restricted, and component (a') may have any viscosity that will permit the formation of a water-based emulsion by the condensation reaction-curing silicone composition. In specific terms, the viscosity will range from 1 mPa.s (centipoise) to that of high-viscosity gums. Preferred viscosities fall in the range of 20 to 100,000 mPa.s (centipoise) and particularly preferred viscosities fall in the range of 20 to 10,000 mPa.s (centipoise).

Component (b') is a crosslinker for the subject condensation reaction-curing silicone composition, and it consists of organohydrogenpolysiloxane having at least 2 silicon-bonded hydrogen atoms in each molecule. The silicon-bonded organic groups in component (b') are monovalent hydrocarbon groups, e.g., alkyl groups such as methyl, ethyl, propyl, and butyl; cycloalkyl groups such as cyclopentyl, or cyclohexyl; aryl groups such as phenyl, tolyl, and xylyl; aralkyl groups such as benzyl, phenethyl, and 3-phenylpropyl; and halohydrocarbon groups such as 3-chloropropyl, or 3,3,3-trifluoropropyl. The silicon-bonded hydrogen may be bonded at any position in the component (b') molecule. The molecular structure of component (b') is not critical and is exemplified by straight chain, cyclic, network, partially branched straight chain, and mixtures of such structures. Straight-chain structures are preferred. The viscosity of component (b') at 25 °C is not specifically restricted, and component (b') may have any viscosity that will permit the formation of a water-based emulsion by the condensation reaction-curing silicone composition. In specific terms, viscosities in the range of 1 to 10,000 mPa.s (centipoise) are preferred. The quantity of component (b') is not specifically restricted as long as it is added in a quantity sufficient to induce cure of the condensation reaction-curing silicone composition. The specifically preferred addition is 0.3 to 100 weight parts component (b') per 100 weight parts component (a').

Component (c') is a condensation-reaction catalyst whose purpose is to accelerate the condensation reaction between the silanol groups in component (a') and the silicon-bonded hydrogen atoms in component (b'). Component (c') is exemplified by the metal salts of organic acids, such as dibutyltin dilaurate, dibutyltin diacetate, tin octanoate, dibutyltin dioctoate, tin laurate, ferric stannooctanoate, lead octanoate, lead laurate, and zinc octanoate; organotitanium compounds such as tetrabutyl titanate, tetrapropyl titanate, and dibutoxytitaniumbis(ethyl acetate); and platinum compounds such as chloroplatinic acid, alcohol solutions of chloroplatinic acid, chloroplatinic acid-olefin complexes, chloroplatinic acid-alkenylsiloxane complexes, platinum black, and platinum-on-silica. No particular restrictions apply to the quantity of component (c') as long as it is added in a quantity sufficient to accelerate the curing reaction of the condensation reaction-curing silicone composition. An addition in the range of 0.01 to 10 weight parts per

100 weight parts component (a') is specifically preferred.

A filler (d') can be added on an optional basis to the condensation reaction-curing silicone composition in order to adjust the fluidity of the composition and/or improve the mechanical strength of the cured silicone powder product. Component (d') is exemplified by reinforcing fillers such as precipitated silica, fumed silica, calcined silica, and fumed titanium oxide, or by nonreinforcing fillers such as quartz powder, diatomaceous earth, aluminosilicates, iron oxide, zinc oxide, and calcium carbonate. Component (d') may be added directly to the condensation reaction-curing silicone composition, or it may be added after a preliminary surface treatment with an organosilicon compound such as hexamethyldisilazane, trimethylchlorosilane, and polydimethylsiloxane.

In order to improve the affinity and adherence between organic resins and the compositions of the invention, our condensation reaction-curing silicone composition may optionally contain a silane coupling agent as component (e'). Component (e') is exemplified by

- vinyltrimethoxysilane,
- vinyltriethoxysilane,
- vinyltris(2-methoxyethoxy)silane,
- vinyltriacetoxysilane,
- 3-chloropropyltrimethoxysilane,
- 3-aminopropyltrimethoxysilane,
- 3-aminopropyltriethoxysilane,
- 3-(2-aminoethyl)aminopropyltrimethoxysilane,
- 3-mercaptopropyltrimethoxysilane,
- 3-glycidoxypropyltrimethoxysilane,
- 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane,
- 3-methacryloxypropyltrimethoxysilane,
- 3-aminopropylmethyldimethoxysilane, and
- 3-glycidoxypropylmethyldimethoxysilane.

Component (e') may be added to the mixing process for components (a'), (b'), and (c'), or it may be preliminarily reacted with component (b'). The quantity of component (e') is not critical, and component (e') should be added in the particular quantity that provides an excellent affinity between the cured silicone powder product and organic resins. The specifically preferred range is 0.1 to 50 weight parts per 100 weight parts component (a').

Other components that may be added to the condensation reaction-curing silicone composition on an optional basis are pigments, heat stabilizers, flame retardants, photosensitizers, and diorganopolysiloxane that carries the silicon-bonded hydroxyl group only at one molecular chain terminal.

A homogeneous water-based emulsion of the curable silicone composition can be prepared by first dispersing the curable silicone composition in water or an aqueous surfactant solution, and by then subjecting this dispersion to the action of an agitator such as a homogenizer, colloid mill, or a mixing device such as an ultrasonic vibrator.

The water-based curable SC emulsion is preferably prepared using surfactant to obtain a very stable emulsion in which the curable silicone composition has a small average particle diameter. Surfactant usable for this purpose is exemplified by nonionic surfactants such as

- polyoxyalkylene alkyl ethers,
- polyoxyalkylene alkylphenyl ethers,
- polyoxyalkylene alkyl esters,
- polyoxyalkylene sorbitan esters,
- polyethylene glycols,
- polypropylene glycols,
- diethylene glycol, and
- the ethylene oxide adducts of trimethylnonanol; anionic surfactants such as
- hexylbenzenesulfonic acid,
- octylbenzenesulfonic acid,
- decylbenzenesulfonic acid,
- dodecylbenzenesulfonic acid,
- cetylbenzenesulfonic acid,
- myristylbenzenesulfonic acid, and
- the sodium salts of the preceding;
- and cationic surfactants such as
- octyltrimethylammonium hydroxide,

dodecyltrimethylammonium hydroxide,
 hexadecyltrimethylammonium hydroxide,
 octyldimethylbenzylammonium hydroxide,
 decyldimethylbenzylammonium hydroxide,
 5 dioctadecyldimethylammonium hydroxide,
 beef tallow trimethylammonium hydroxide, and
 cocotrimethylammonium hydroxide.

These may be used singly or as mixtures of two or more selections. Particularly preferred is the use of two nonionic surfactants chosen such that the hydrophiliclipophilic balance number (HLB) of one surfactant is less than 10, the HLB of the other is at least 10, and the difference in their HLB values is at least 5. The use of such a surfactant combination yields smaller average particle diameters for a curable silicone composition in a water-based emulsion. The quantity of surfactant addition is not critical, but it is preferably added at 0.1 to 20 weight parts per 100 weight parts curable silicone composition. It is particularly preferred to be added at 0.5 to 8 weight parts per 100 weight parts curable silicone composition.

15 The amount of water addition is also not specifically restricted. The preferred water addition is 40 to 2,000 weight parts per 100 weight parts curable silicone composition and the particularly preferred water addition is 40 to 1,000 weight parts water per 100 weight parts of curable silicone composition. It becomes difficult to form the water-based curable SC emulsion when water is added at less than 40 weight parts per 100 weight parts. At the other extreme, the use of more than 2,000 weight parts water causes the process to have a poor productivity. The water should have a low content of metal and halogen ions, and conductivity values not exceeding 1 microS/cm are preferred. Ion-exchanged water with a conductivity not exceeding 0.5 microS/cm is particularly preferred.

A water-based dispersion of the cured silicone powder (A) is then produced by curing the curable silicone present in the water-based emulsion. This cure may be effected by allowing said water-based emulsion to stand at room temperature or by heating the water-based emulsion. If heating the water-based curable SC emulsion, the preferred heating temperature should not exceed 100°C, while particularly preferred temperatures fall in the range of 40°C to 95°C. The techniques for heating the water-based curable SC emulsion are by direct heating of the water-based emulsion or by adding the water-based emulsion to hot water.

30 The average particle diameter of the cured silicone powder (A) prepared above must be 0.1 to 200 micrometers, and is preferably 0.5 to 80 micrometers. The amorphous silica micropowder does not become satisfactorily anchored or immobilized on the surface of cured silicone powder with an average particle diameter below 0.1 micrometer, while the final cured silicone powder composition has a strongly reduced fluidity and dispersibility when the average particle diameter exceeds 200 micrometers.

35 The preparative process of the invention continues with the addition of amorphous silica micropowder (B) to the water-based dispersion of cured silicone powder (A) in order to prepare a water-based dispersion of components (A) and (B). The component (B) used in our invention must be an amorphous silica micropowder that has an average particle diameter no greater than 1 micrometer and a surface silanol group density of at least 2 silanol groups per one nm² (100 square angstroms). When component (B) has a surface silanol group density below 2 silanol groups per one nm² (100 square angstroms), the hydrophilicity of this component is diminished to the point that it cannot be homogeneously dispersed, and it undergoes phase separation when added to the water-based dispersion of cured silicone powder (A). Component (B) must have an average particle diameter that does not exceed 1 micrometer, and preferably has an average particle diameter in the range of 0.001 to 0.1 micrometer. Component (B) will not be strongly anchored on the surface of component (A) when the average particle diameter of component (B) exceeds 1 micrometer. 45 The shape of component (B) is not critical, but it is preferably spherical. The amorphous silica micropowder of component (B) is exemplified by dry-process, electric arc, and wet-process amorphous silica micropowders. Fumed silica, which is prepared by a dry process, is particularly preferred as component (B).

The silanol group density on the surface of the amorphous silica micropowder (B) can be determined from the specific surface of component (B) and the silanol group titer. The latter value can be determined by drying component (B) at 120°C for 3 hours in a vacuum at or below 2 kPa (15 mmHg) and then reacting the silanol groups on the surface of component (B) with lithium aluminum hydride and quantitating the evolved hydrogen gas.

55 The quantity of component (B) addition in the process of our invention is not critical, and it should be added in a quantity appropriate for immobilization on the surface of component (A). In specific terms, component (B) is preferably added at 0.1 to 30 weight parts per 100 weight parts component (A). Component (B) is preferably added at 1 to 15 weight parts when the average particle diameter of component (A) is 0.1 to 10 micrometers, and is preferably added at 0.5 to 10 weight parts when the

average particle diameter of component (A) is 10 to 200 micrometers.

No particular restrictions apply to the technique for mixing the amorphous silica micropowder (B) into the water-based dispersion of cured silicone powder (A). Examples include the direct addition of component (B) to the water-based dispersion of component (A) and the preliminary preparation of a water-based dispersion of component (B) which is then added to the water-based dispersion of component (A).

After preparation of the water-based dispersion of cured silicone powder (A) and amorphous silica micropowder (B), the process of this invention continues with the heating of said dispersion, which brings about a strong immobilization or anchorage of component (B) on the surface of component (A) through interactions in the water between the silanol groups on the surface of component (B) and the silanol, silicon-bonded hydrogen, and alkoxy on the surface of component (A). No specific restrictions apply to the temperature for heating the water-based dispersion of components (A) plus (B). The preferred temperature range is 40 °C to 95 °C and the particularly preferred temperature range is 60 °C to 90 °C.

The preparative process of our invention concludes with removal of the water from the water-based dispersion of cured silicone powder (A) and amorphous silica micropowder (B) to yield a cured silicone powder that consists of component (A) whose surface carries immobilized component (B). The technique for removing water from the water-based dispersion is not specifically restricted, and the known methods can be used for the present purpose. For example, removal is readily effected through the use of an air or vacuum drier, a forced convection oven, a spray drier, and so forth.

The amorphous silica micropowder (B) is firmly immobilized or anchored on the surface of the cured silicone powder (A) in the cured silicone powder afforded by our preparative process. As a result, the cured silicone powder does not readily shed component (B) even when subjected to shear forces. The strength of attachment of the amorphous silica micropowder (B) on the surface of the cured silicone powder (A) can be easily determined by application of high shear force to the cured silicone powder product in a medium such as water, or organic solvent. The cured silicone powder of this invention exhibits little tendency to aggregate or undergo blocking and contains only very small quantities of secondary aggregates. Therefore it will not produce clogging in equipment or hoppers during storage. Moreover, due to its excellent fluidity and excellent dispersibility in organic resins and organic solvents (i.e., non-silicone systems), our cured silicone powder can be thoroughly dispersed into cosmetics, thermosetting organic resins, and thermoplastic organic resins.

EXAMPLES

The composition of the invention and its preparative process are described in greater detail hereinafter through working examples. The viscosity values reported in the examples were measured at 25 °C, and the properties of the cured silicone powder were measured as follows.

Average particle diameter

This was measured using an image processor connected to an optical microscope.

Fluidity of the cured silicone powder composition

50 g of cured silicone powder composition (passes 40 mesh or 373 micrometers) was poured from a height of 20 cm and the angle of repose (i.e., base angle of the cone formed) was measured.

Aggregation of the cured silicone powder composition

Using an air-jet sieve from the Alpine Company, the % on-mesh was measured with a 325 mesh sieve (mesh opening = 44 micrometers).

Blocking of the cured silicone powder composition

100 g of the cured silicone powder composition was placed in a tube with a cross section of 10 cm x 10 cm, and a load of 1 kgf was applied from the top. After standing for 2 days, the load was withdrawn and the sample was divided into 10 portions. Using an air-jet sieve from the Alpine Company, a 10 g portion of the cured silicone powder composition was passed through 150 mesh (mesh opening = 105 micrometers) over 5 minutes, and the % on-mesh was then measured.

Dispersibility of the cured silicone powder composition

1 g of cured silicone powder composition and 50 mL toluene were placed in a lid-equipped 100 mL mayonnaise bottle. The bottle was shaken 50 times and thereafter allowed to stand for 10 hours.
 5 Aggregates of the cured silicone powder composition were then measured using an image processor connected to an optical microscope.

Silica separation ratio for the cured silicone powder composition

10 2.0 g of cured silicone powder composition and 100 mL acetone were stirred for 10 minutes at 4,000 rpm in a homomixer, and the cured silicone powder composition was thereafter separated by filtration. The cured silicone powder composition was then washed with acetone, air-dried, and added to 50 mL brine with a specific gravity of 1.3. This was mixed for 10 minutes at 4,000 rpm using a homomixer and then centrifuged. The amount of silica sedimenting as the lower layer was measured, and this weight was
 15 reported as a percentage of the silica input for the cured silicone powder composition.

Sodium and halogen ion concentrations in the cured silicone powder composition

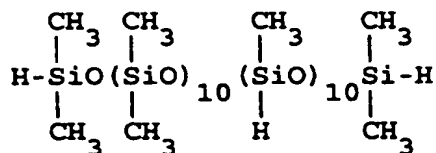
2.0 g of cured silicone powder composition and 50 g ion-exchanged water (conductivity = 0.4 microS/cm) were introduced into a pressure cooker and heated at 121 °C for 20 hours in order to extract ionic impurities in the cured silicone powder composition into the water. The sodium and halogen ion concentrations in this aqueous extract were measured by ion chromatography.

Moisture resistance of resin-sealed semiconductor devices

25 A cured silicone powder composition-filled thermosetting epoxy resin was prepared and used to fabricate 20 resin-sealed semiconductor devices (chip size = 36 mm², package thickness = 2.0 mm). These resin-sealed semiconductor devices were heated for 500 hours at 121 °C under pressure cooker test conditions, and the number of resin-sealed semiconductor devices was then counted in which aluminum
 30 interconnects had been broken.

EXAMPLE 1

The following were blended to homogeneity at -10 °C to give a composition (I): 50 weight parts of dimethylvinylsiloxyl-endblocked dimethylpolysiloxane (viscosity = 800 mPa.s (centipoise), vinyl equivalent weight = 8,000, sodium ion concentration ≤ 2 ppm, halogen ion concentration ≤ 5 ppm), 11 weight parts of dimethylsiloxane-methylhydrogensiloxane copolymer (viscosity = 20 mPa.s (centipoise), sodium ion concentration ≤ 2 ppm, halogen ion concentration ≤ 5 ppm) with the following formula



2 weight parts of allyl glycidyl ether, and 2 weight parts of vinylcyclohexene monoxide.

Composition (I) was then blended to homogeneity at 5 °C with 50 weight parts of dimethylvinylsiloxyl-endblocked dimethylpolysiloxane as described above and sufficient isopropanolic chloroplatinic acid solution to provide 20 ppm platinum metal based on the total amount of dimethylvinylsiloxyl-endblocked dimethylpolysiloxane. Into the resulting blend were rapidly mixed 200 weight parts of pure water at 25 °C (conductivity = 0.2 microS/cm) and 4 weight parts polyoxyethylene nonylphenyl ether (HLB = 13.1). Passage through a homogenizer (300 kg/cm²) then yielded a homogeneous water-based emulsion of a curable silicone. This water-based curable SC emulsion was held at 30 °C for 6 hours, which resulted in curing of the curable silicone and the production of a water-based cured SP dispersion. 5 weight parts of fumed silica (surface silanol group density = 4.2 silanol groups per 100 one nm² (square angstroms), primary particle diameter = 20 millimicrons) was subsequently added to the water-based cured SP

dispersion, which, after dispersing to homogeneity, was then heated for 1 hour at 80 °C. The resulting water-based dispersion of cured silicone powder + fumed silica was dried in a spray drier, and 110 weight parts of a cured silicone powder composition was recovered by cyclone separation.

5 COMPARATIVE EXAMPLE 1

The procedure of Example 1 was followed, but in this case substituting the fumed silica used in Example 1 with a dimethyldichlorosilane-hydrophobicized fumed silica (surface silanol group density = 1.2 silanol groups per one nm² (100 square angstroms), primary particle diameter = 20 millimicrons). 105 weight parts of cured silicone powder composition was recovered. When the hydrophobicized fumed silica was added in this case to the water-based cured SP dispersion, the silica floated on the surface of the water-based dispersion and a homogeneous dispersion could not be prepared. In addition, the hydrophobicized fumed silica could not be recovered by cyclone during spray drying of the water-based dispersion of cured silicone powder + hydrophobicized fumed silica. Rather, a micropowder that was discharged in the form of a white cloud was collected using a venturi scrubber, and this was confirmed to the hydrophobicized fumed silica.

COMPARATIVE EXAMPLE 2

20 The procedure of Example 1 was followed, but in this case adding the fumed silica to the water-based curable SC emulsion in order to prepare a water-based emulsion of curable silicone + fumed silica. This water-based emulsion was held for 7 hours at 25 °C and processing in the spray drier was then attempted; however, uncured curable silicone composition had sedimented and drying could not be carried out.

25 EXAMPLE 2

A curable silicone was prepared from 50 weight parts of dimethylvinylsiloxyl-terminated dimethylpolysiloxane (viscosity = 400 mPa.s (centipoise), vinyl equivalent weight = 5,400, sodium ion concentration ≤ 2 ppm, halogen ion concentration ≤ 5 ppm), 1.5 weight parts of trimethylsiloxyl-terminated methylhydrogenpolysiloxane (viscosity = 20 mPa.s (centipoise), silicon-bonded hydrogen equivalent weight = 67, sodium ion concentration ≤ 2 ppm, halogen ion concentration ≤ 5 ppm), 7.5 x 10⁻³ weight parts of tetramethyltetravinylcyclotetrasiloxane, and sufficient isopropanolic chloroplatinic acid solution to provide 120 ppm platinum metal based on the total weight of the dimethylvinylsiloxyl-terminated dimethylpolysiloxane. 0.25 weight parts of polyoxyethylene nonylphenyl ether (HLB = 5.7) was added to this curable silicone mixture. Into the resulting mixture was then dripped, over a period of approximately 5 minutes while stirring, an aqueous solution composed of 1 weight part polyoxyethylene octylphenyl ether (HLB = 18.1) and 10 weight parts pure water with a conductivity of 0.2 microS/cm. After stirring for approximately 1 hour at 600 rpm, the mixture was passed through a colloid mill to produce a thick water-based emulsion of a curable liquid silicone. A homogeneous water-based emulsion of the curable liquid silicone was then prepared by the addition of the aforesaid emulsion while stirring to sufficient pure water to yield a 50 weight% silicone component. The curable silicone was cured by holding the water-based curable SC emulsion overnight, thereby yielding a water-based cured SP dispersion. 50 weight parts of 10% water-based dispersion of fumed silica (surface silanol group density = 4.2 silanol groups per one nm² (100 square angstroms), primary particle diameter = 20 millimicrons) was added to the water-based cured SP dispersion with stirring to homogeneity. Heating for 1 hour at 70 °C then yielded a water-based dispersion of cured silicone powder + fumed silica. This dispersion was dried in a spray drier, as a result of which approximately 58 weight parts cured silicone powder composition was recovered by cyclone.

COMPARATIVE EXAMPLE 3

50 A cured silicone powder composition was prepared as in Example 2, but in this case omitting the fumed silica that was used in Example 2.

COMPARATIVE EXAMPLE 4

55 50 weight parts of cured silicone powder was prepared by the procedure in Example 2, but in this case replacing the fumed silica used in Example 2 with 27 weight parts colloidal silica (concentration = 20 weight%, average particle diameter = 30 millimicrons, sodium ion concentration = 0.03%).

EXAMPLE 3

A curable silicone composition was prepared from 50 weight parts of silanol-endblocked dimethylpolysiloxane (viscosity = 40 mPa.s (centipoise), hydroxyl equivalent weight = 450, sodium ion concentration ≤ 2 ppm, halogen ion concentration ≤ 5 ppm), 4.0 weight parts of trimethylsiloxy-endblocked methylhydrogenpolysiloxane (viscosity = 20 mPa.s (centipoise), silicon-bonded hydrogen equivalent weight = 67, sodium ion concentration ≤ 2 ppm, halogen ion concentration ≤ 5 ppm), and 0.75 weight parts dibutyltin dilaurate. While maintaining this curable silicone composition at 10°C, it was mixed into 250 weight parts pure water (conductivity = 0.2 microS/cm) and 3 weight parts polyoxyethylene nonylphenyl ether (HLB = 13.1), and the resulting mixture was passed through a homogenizer to yield a homogeneous water-based emulsion of the curable silicone composition. The water-based curable SC emulsion was held at 25°C for 10 hours in order to cure the curable silicone composition, thereby yielding the water-based dispersion of a cured silicone powder. 8 weight parts of fumed silica (surface silanol group density = 2.5 silanol groups per one nm² (100 square angstroms), primary particle diameter = 10 millimicrons) was added to this water-based cured SP dispersion with stirring to homogeneity. Heating at 60°C for 30 minutes gave a water-based dispersion of cured silicone powder + fumed silica. Drying this water-based dispersion of cured silicone powder + fumed silica in a spray drier resulted in the recovery by cyclone of approximately 55 weight parts of a cured silicone powder composition.

COMPARATIVE EXAMPLE 5 (corresponds to Comparative Example 2 from JP-A 4-348143)

A water-based curable SC emulsion was prepared as in Example 1. The direct addition of 500 weight parts of hot water (90°C) to this emulsion and standing for a day at room temperature yielded the water-based dispersion of a cured silicone powder. 1.1 weight parts of fumed silica as described in Example 1 was mixed to homogeneity into this water-based cured SP dispersion to yield a dispersion of cured silicone powder + fumed silica. This water-based dispersion was then dried in a spray drier and a cured silicone powder was recovered by cyclone. During this process white smoke composed of the fumed silica was observed coming from the bag filter.

COMPARATIVE EXAMPLE 6

A cured silicone powder was prepared as in Example 1, but in this case without using the fumed silica that was used in Example 1. 5 weight parts of fumed silica as described in Example 1 was added to this cured silicone powder, and mixing to homogeneity in a Henschel mixer then yielded a cured silicone powder composition.

APPLICATION EXAMPLE 1

The following were mixed to homogeneity on a two-roll mill at 90°C: 75 weight parts of ortho-cresol novolac epoxy resin (softening point = 80°C, epoxy equivalent weight = 220), 26 weight parts of the cured silicone powder composition prepared in Example 1, 260 weight parts of fused silica, 1 weight part carnauba wax, 35 weight parts of phenol novolac resin, 0.6 weight parts of triphenylphosphine, and 0.5 weight parts of 3-glycidylpropyltrimethoxysilane. This blend was then ground to yield a curable epoxy resin composition. The cured silicone powder composition was uniformly dispersed in the curable epoxy resin composition. The curable epoxy resin composition was then used to fabricate 20 resin-sealed semiconductor devices. The moisture resistance of these resin-sealed semiconductor devices was rated as excellent and there were no failures found (0/20).

APPLICATION EXAMPLE 2

A curable epoxy resin composition was prepared as in Application Example 1, but in this case using the cured silicone powder composition prepared in Comparative Example 4 in place of the cured silicone powder composition of Example 1. It was determined that this curable epoxy resin composition contained aggregates of the cured silicone powder composition. The curable epoxy resin composition was then used to fabricate 20 resin-sealed semiconductor devices. The moisture resistance of these resin-sealed semiconductor devices was rated as poor and there were 18 failures (18/20).

The test results of the examples and comparative examples are presented in Table 1.

TABLE 1

	Invention Examples			Comparative Examples					
	Example 1	Example 2	Example 3	Comp. Ex. 1	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6	
average particle diameter (micrometers)	3	1	2	3	1.5	4	3	3	
angle of repose (degrees)	32	34	30	55	61	32	43	32	
aggregation (%)	< 0.1	< 0.1	< 0.1	52	58	< 0.1	34	21	
blocking (%)	0.1	0.1	0.1	2	90	5	75	12	
dispersibility (mm)	< 0.5	< 0.5	< 0.5	5	9	< 0.5	6	5	
silica separation ratio (%)	11	5	2	99 - 100	-	85	95	98	
sodium ion concentration (ppm)	0.3	0.5	1.0	0.8	0.5	35	0.3	0.3	
halogen ion concentration (ppm)	5	7	10	10	8	17	5	5	

Claims

1. A composition comprising:

(A) a cured silicone powder having a number average particle diameter of 0.1 to 200 micrometers; and

(B) an amorphous silica micropowder having an average particle diameter not exceeding one micrometer and a surface silanol group density of at least 2 silanol groups per one nm² (100 square angstroms), characterized in that said silica micropowder is immobilized on the surface of said cured silicone powder.

2. The composition according to claim 1, wherein said powder (A) has a number average particle diameter of 0.1 to 10 micrometers and from 1 to 15 parts by weight of said silica micropowder (B) is present for each 100 parts by weight of said powder (A).
- 5 3. The composition according to claim 1, wherein said powder (A) has a number average particle diameter of 10 to 200 micrometers and from 0.5 to 10 parts by weight of said silica micropowder (B) is present for each 100 parts by weight of said powder (A).
- 10 4. The composition according to claim 1, wherein said powder (A) is a cured polydimethylsiloxane powder.
5. The composition according to claim 1, further comprising an organic resin.
- 15 6. The composition according to claim 9, wherein said organic resin is an epoxy resin.
7. A process for preparing a cured silicone powder composition comprising:
(I) preparing a water-based dispersion of the composition of claim 1;
(II) heating said water-based dispersion; and
(III) removing the water from said dispersion.
- 20 8. The process according to claim 7, wherein said powder (A) is a cured polydimethyl siloxane and from 0.1 to 30 parts by weight of said silica micropowder (B) are present for each 100 parts by weight of said cured silicone powder (A).

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European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 94 11 5689

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US-A-5 153 238 (BILGRIEN ET AL) * column 6, line 31 - line 38 * * column 8, line 67 - column 9, line 4 * * column 9, line 34 * ---	1-5,7,8	C08J3/12
X	EP-A-0 548 969 (DOW TORAY) * column 1, line 20 - line 26 * * column 1, line 47 - line 50 * * column 3, line 46; claim 1 * ---	1-4,7,8	
A	EP-A-0 379 451 (RHONE-POULENC) * column 8, line 15 - line 21 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C08J
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 24 January 1995	Examiner Lentz, J
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X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

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